

Epoxy and polyester-based vitrimers and composites

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Vitrimers, invented in 2011 by the group of Leibler,¹ are chemically crosslinked networks characterized by the presence of exchangeable links, a feature that allows to change topology while keeping the integrity of the network. Vitrimers show unusual combination of properties: they are both insoluble and processable, and flow in the same way as glass at high temperature.

This makes them fundamentally recognized as a third and new class of polymeric materials, alongside thermoplastics and thermosets, and on a practical level as a new means of controlling and resolving problems of (re)processing, chemical strength and thermal resistance of materials and composites.

This will be illustrated through two examples : *i*) manufacture of glass-fiber / epoxy vitrimers composite plates and their assembly by autogeneous welding and *ii*) crosslinking an industrial thermoplastic resin using epoxy-vitrimer chemistry.

Prototypes of vitrimers were based on exchangeable links by transesterification and implemented by using classical epoxy chemistry. As epoxies are ubiquitous in high performance composites, the question addressed here is to examine to what extent the original properties of vitrimer are maintained in materials containing more than 50% by weight of reinforcing fibers. To answer this question, we analyze quantitatively the bond strength of epoxy vitrimer based composite plates made by resin transfer molding and compare them to their non-vitrimer counterparts made of a standard thermoset epoxy, **Figure 1**.

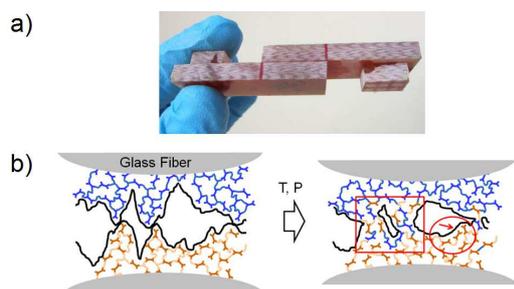


Figure 1. The implementation and the welding of vitrimer matrix composite parts (a) illustrates the insertion of this chemistry in a complex chain of transformations. Formation of new chemical bonds via exchanges and improvement of the contact allowed by the characteristic flow properties of the vitrimers both contribute to the adhesion (b).

It is demonstrated that only epoxy vitrimer samples show substantial bond strength and the ability to be repeatedly welded thanks to the exchange reactions which promote improved surface conformity and chemical bonding between the adherands at the joint interface. This opens the way towards joining composite parts without adhesives nor mechanical fasteners.¹

Polybutylene terephthalate, PBT is characterized by a high degree of crystallinity, a high melting point and rapid crystallization. One of its limitations is that just above the melting point (230 °C) any mechanical strength disappears and the polymer tends to drip under its own weight. In demanding applications, it is necessary to use crosslinked PBT but the existing crosslinking processes are complex and the polymer obtained is not recyclable. In the process that we envisioned, PBT is modified by epoxy resins in the presence of a transesterification catalyst, directly into an extruder. To devise an effective formulation we studied in detail the exchange reactions and catalysis in model systems and in the polymer. The polymer thus obtained maintains the essential properties of a semi-crystalline thermoplastic polymer and acquires the new properties of vitrimers such as heat resistance, mechanical strength and solvent resistance. Transformation of ordinary PBT into a vitrimer could open up new areas of application for PBT.

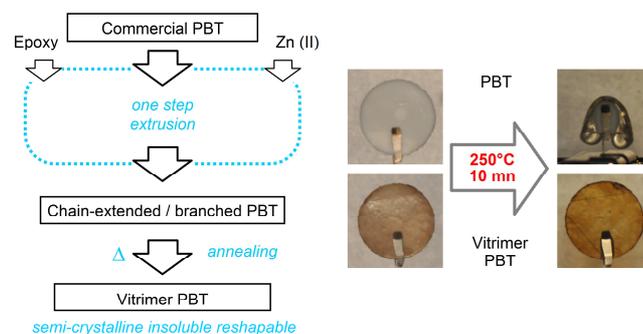


Figure 2. Strategy used to obtain a vitrimer PBT by an easily upscalable means. In the right part, we show how this transformation enhance the heat resistance of PBT above its melting point.

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